Adventures in Ionic Liquid Architecture

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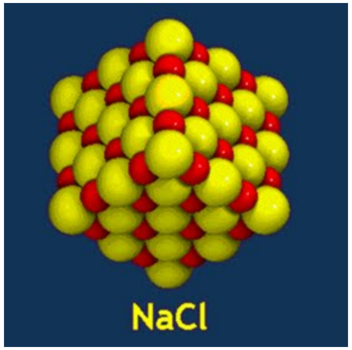
IONIC COMPOUNDS

- *Composed of + (cations) and - (anions)*
- *Ions have similar sizes and pack closely together into a crystal*
- *Generally thought to be high melting crystalline solids like NaCl which melts when heated above 800 ^{o}C (molten salt)*

Ionic lattice of Na^{+} cations and Cl^{-} anions.

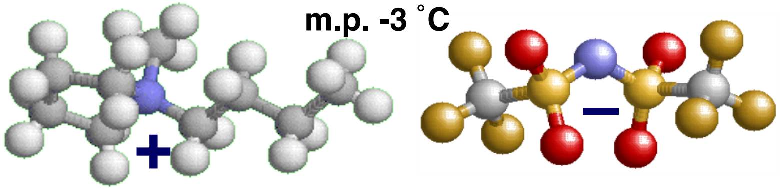
$$|\mathbf{F}| = k_e \frac{|q_1 q_2|}{r^2}$$

MP: 801 ^{o}C



NaCl (melts at 801 ˚C)

Ionic liquids are liquid salts

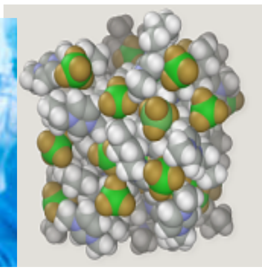


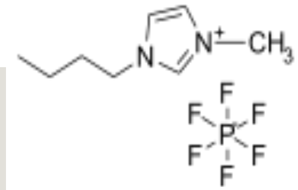
What are ionic liquids?

- ***Salts that are liquid at or near room temperature (< 100 ^{0}C)***

$$|\mathbf{F}| = k_e \frac{|q_1 q_2|}{r^2}$$

MP: 6.5





1--butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6)

- ***Composed of bulky ions with low molecular symmetry***

- ***Intentionally designed to make bad crystals and good liquids by mismatching the sizes of cations and anions***

- ***Designer solvents- Can chemically modify ions and mix and match them as needed to give the desired properties***

Ionic Liquids – "Extreme Solvents"

Electrostatic attraction is still strong enough to make vapor pressure ~0.

If it can't evaporate, it can't burn.

Combine specific ions to give desired properties.

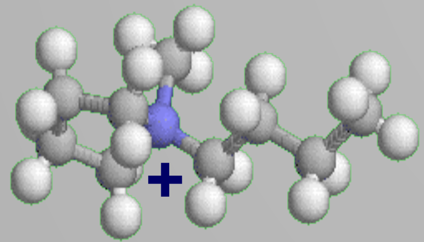
Control solubility of solids and liquids:

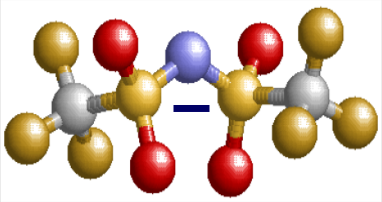
Phase separation (like oil and water).

Easy separation of products.

Make liquid easy to reuse/recycle.

- Inherently safer.
- More economical.
- Less environmentally burdensome.





- Ionic liquid properties lie at the edge of or beyond those of normal liquids.
- Wide Electrochemical range (≤ 6 V)
- Wide Liquid range (≤ 250° C)
- Very low vapor pressure
- Viscosity (higher than normal)
- Dissolve polar, non-polar, biopolymers
- Intrinsically conductive

Ionic liquids provide a path to new science and technology.

Slide courtesy of Jim Wishart

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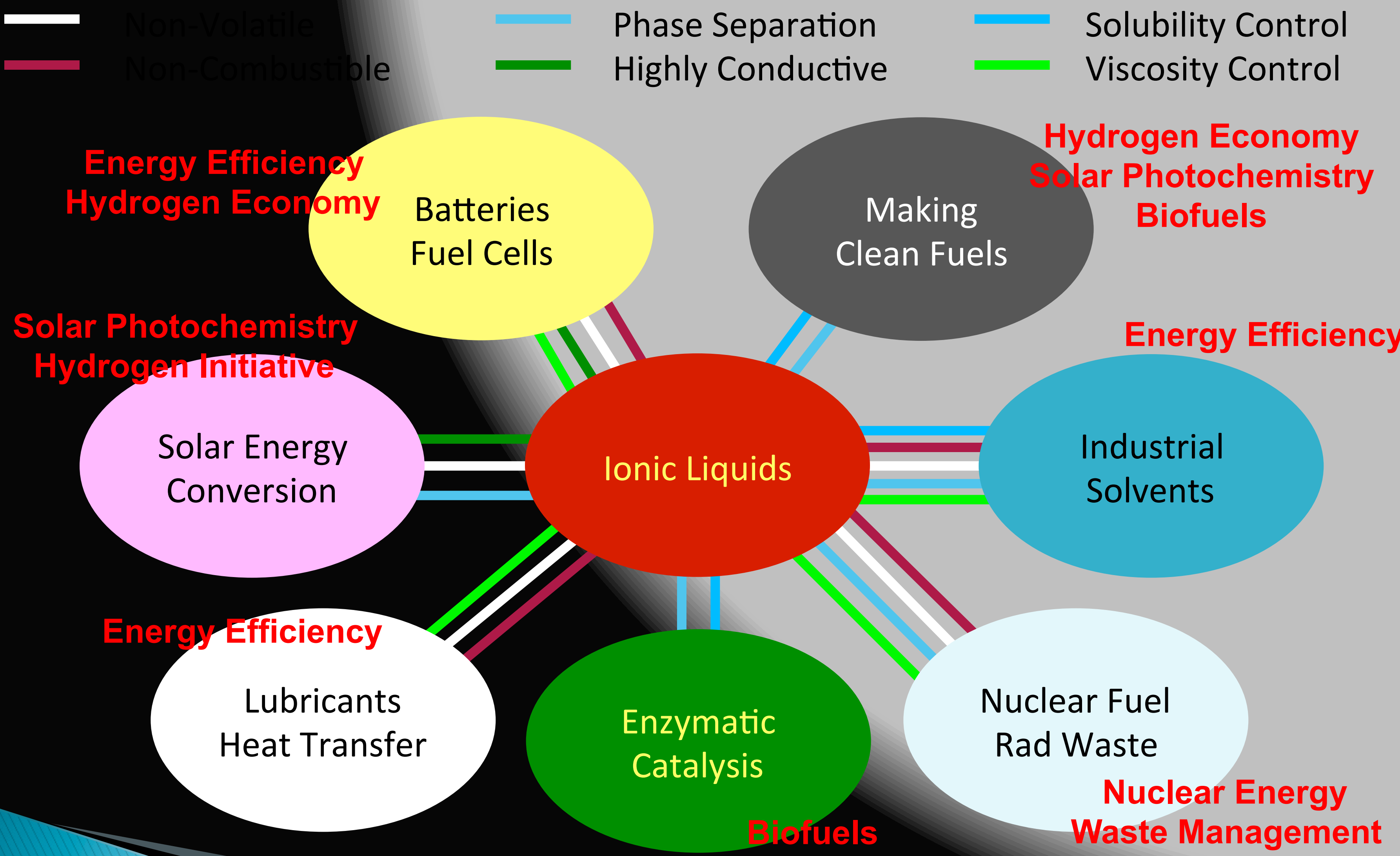
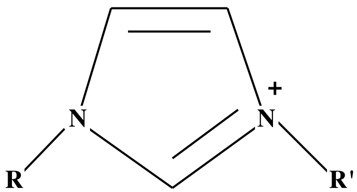
Ionic Liquids and Energy: Designer Solvents for a Sustainable World



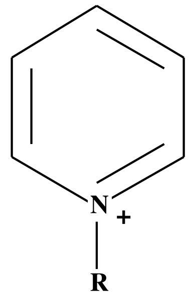
Slide courtesy of Jim Wishart

Chemical Makeup of Common Ionic Liquids

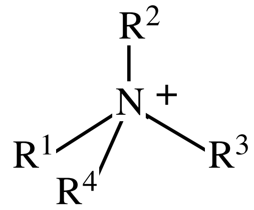
Cations



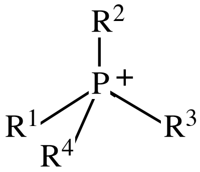
N-alkyl-N'-alkyl'-imidazolium



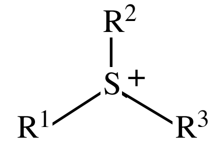
N-alkyl-Pyridinium



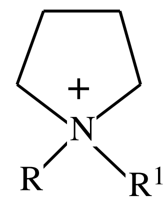
Tetraalkyl-ammonium



Tetraalkyl-phosphonium



Trialkylsulfonium



N-alkyl-N-alkyl'-pyrrolidinium

Anions

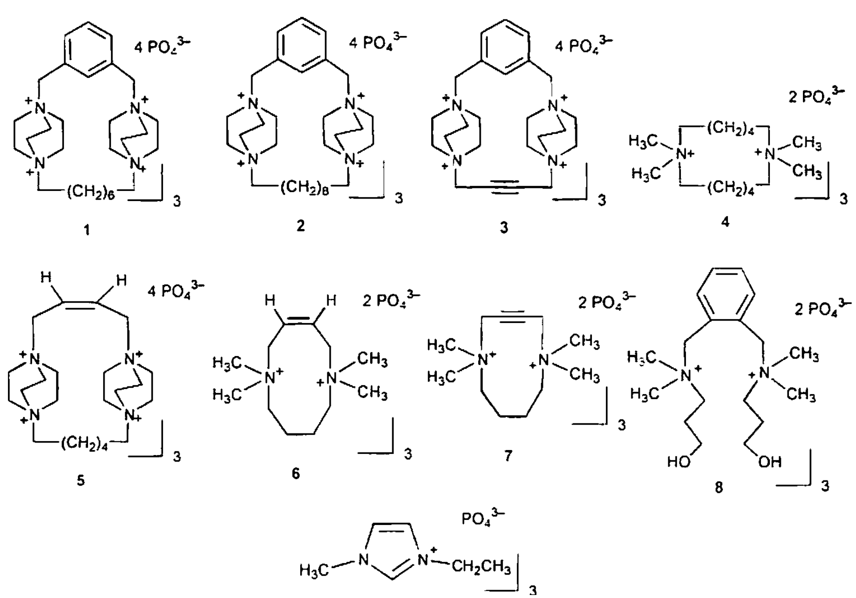
- ***Tetrachloroaluminate*** $[AlCl_4]^-$
- ***Tetrafluoroborate*** $[BF_4]^-$
- ***Hexafluorophosphate*** $[PF_6]^-$
- ***Chloride*** Cl^-
- ***Others:*** $CF_3CO_2^-$, $CH_3CO_2^-$, $CH_3SO_3^-$
- ***Bis(trifluoromethanesulfonyl)imide*** $[(CF_3SO_2)_2N]^-$
- ***Trifluoromethanesulfonate*** $[CF_3SO_3]^-$
- ***Dicyanamide*** $[(CN)_2N^-]$

Beginning collaborations with BNL

Polycations. Part X. LIPs, a new category of room temperature ionic liquid based on polyammonium salts

Sharon I. Lall, Danny Mancheno, Steve Castro, Valbona Behaj, JaimeLee Iolani Cohen and Robert Engel*

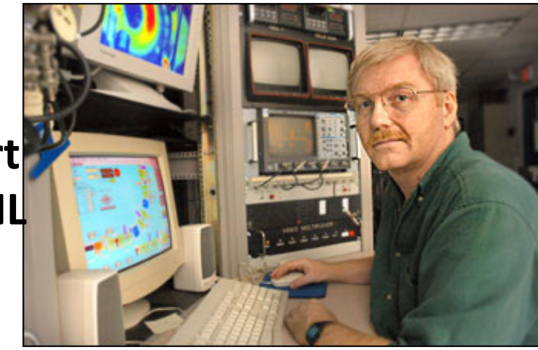
Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Boulevard, Flushing, NY 11367, USA. E-mail: robert_engel@qc.edu



Chem. Commun., 2000, 2413–2414

Robert Engel

James Wishart
Chemistry, BNL



- My first publication on Ionic Liquids
- This paper caught the attention of BNL scientist: Dr. James Wishart
- He invited us to a meeting at BNL in January 2001

Continued collaborating at BNL as a graduate student

• Spent 1-2 nights in the BNL dorms a few times during the semester/ winter: Made designer ILs to order; published a paper

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Radiation Physics and Chemistry 72 (2005) 99–104

Radiation Physics and Chemistry

Effects of functional group substitution on electron spectra and solvation dynamics in a family of ionic liquids

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Received 30 November 2003; accepted 22 December 2003

Research Focus

- **Synthesize structurally unique ionic liquids**
- **Investigate their physical properties**
- **Correlate structure with function so that physical properties can be predicted from structure**
- **Design or manipulate the structure of the IL to provide desired properties**
- **Design ILs for sustainable energy applications (batteries, Supercapacitors, Nuclear fuel reprocessing, Solar Energy conversion) and probing the nanostructure of ILs through collaboration**

- **ILs for cellulose dissolution: Pretreatment for biofuel production**
- **Investigate toxicity properties and correlate toxicity with structure**
- **Biodegradation of ILs**

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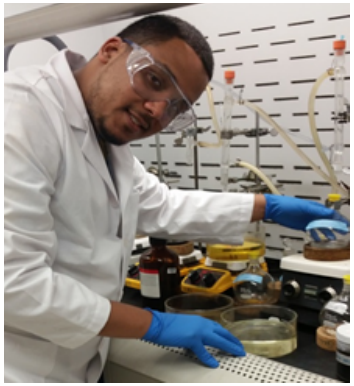
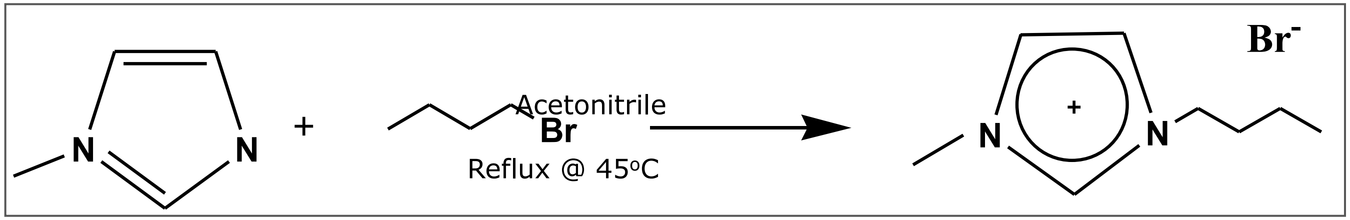
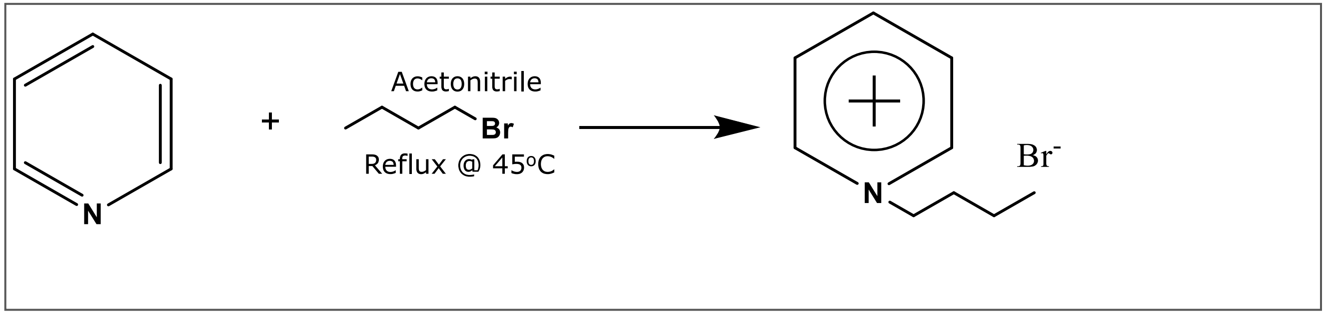
Synthesis of cations in ILs

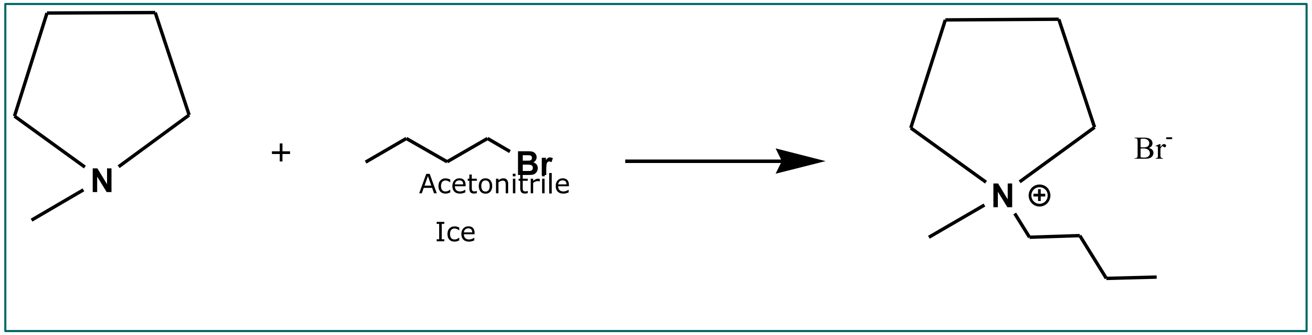


Rahonel Fernandez





Chanele Rodriguez



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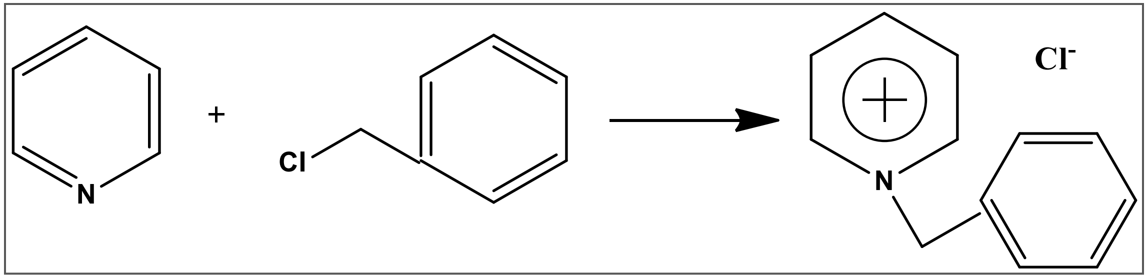
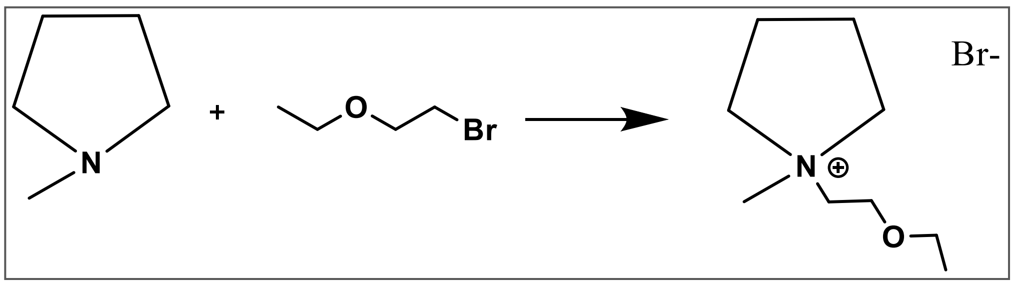
Synthesis of functionalized cations for ILs

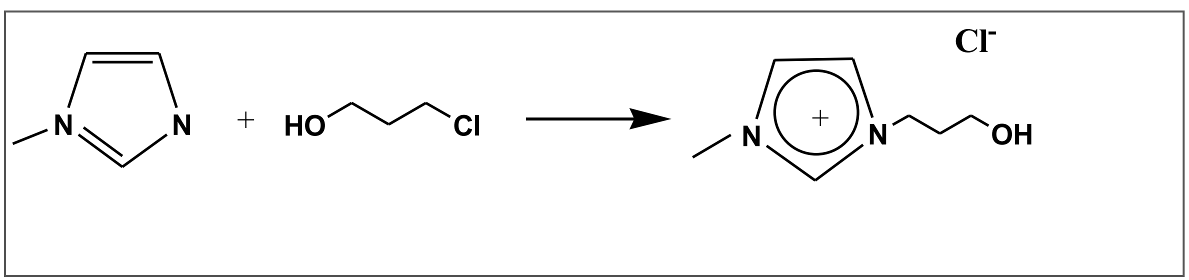
Sofiya Penkhasova

Vanessa Hernandez

Kdarieyaime Jaleesa







Heidi Martinez

Annu Ipe

Carolyn Spence

Microwave synthesis of cations

- Allows for fast and efficient synthesis with minimum use of solvent
- Minimizes Waste
- Reactants are volatile, product salt is not.
Pressure can be used to gauge progress of the reaction.

Slide obtained from collaborator Jim Wishart

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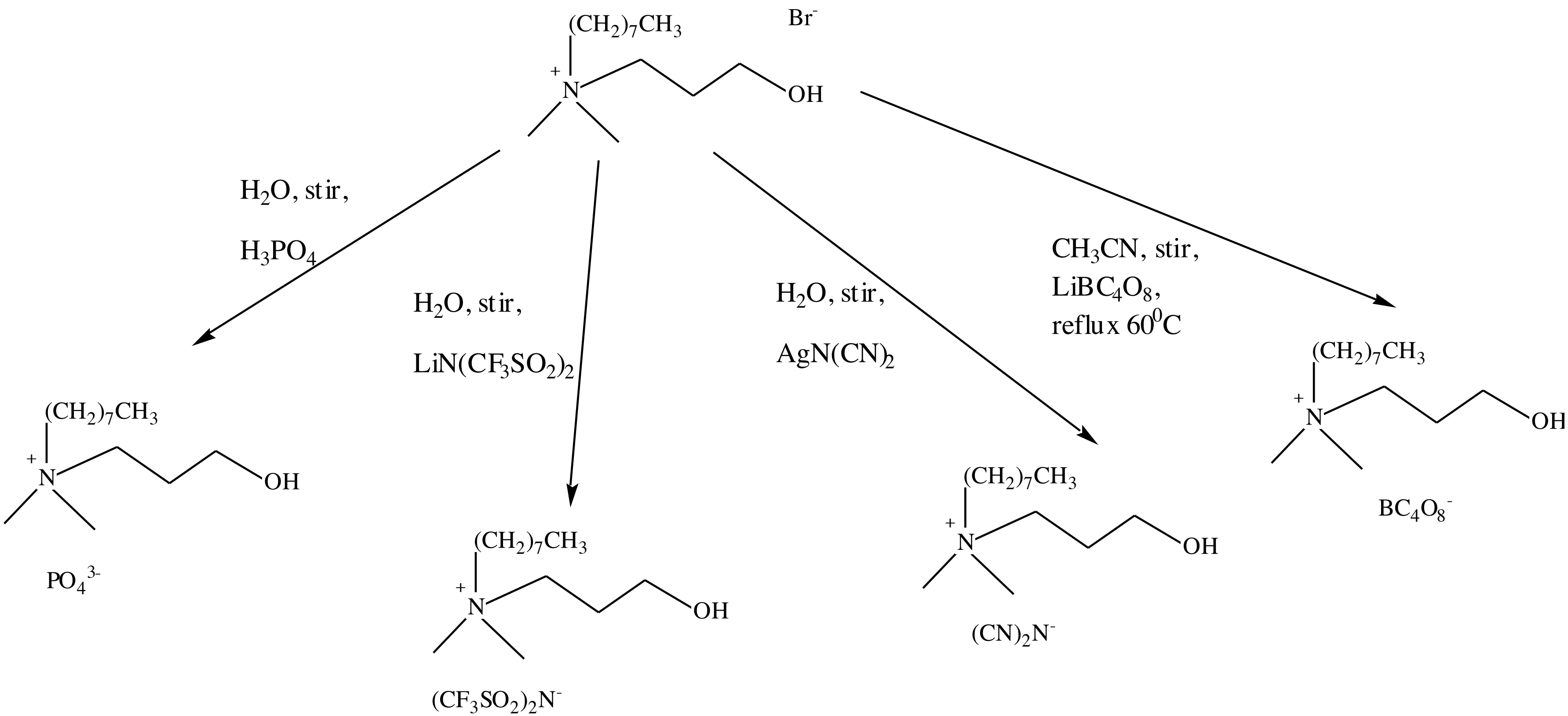
Reaction scheme for synthesizing ionic liquids from a halide salt precursor



S. Lall et. al, J. Chem. Soc., Chem. Commun., 2413 (2000)

S. Lall et. al. Synthesis, 11, 1530-1540 (2002)

J. Wishart, S. Lall-Ramnarine, et. al, Radiat. Phys. Chem. 72, 99-104 (2005)

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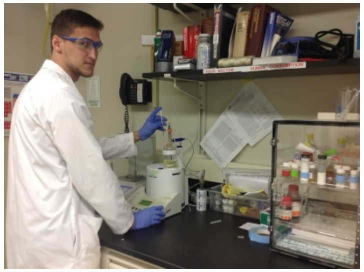
Purification of ILs

- Washing with ethylacetate, diethylether, acetonitrile
- Activated charcoal if colorless ILs are desired
- Testing for and removing residual halide ($AgNO_3$ and washing with water)
- Testing for and removing residual water (KF Titrator, TGA and drying in vac. oven)

- Structures are confirmed using H-1, C-13 and P-31 NMR

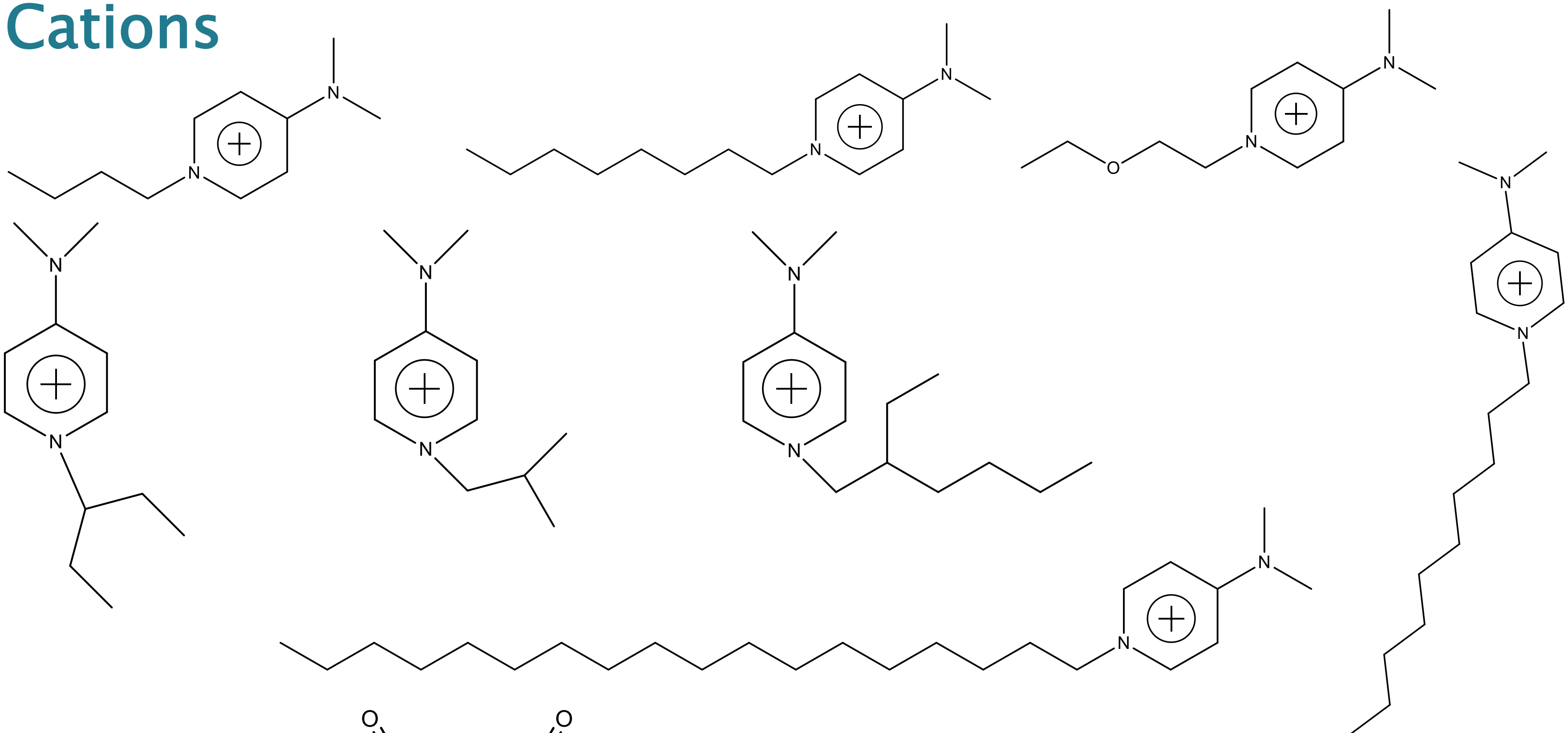


Physical properties investigated

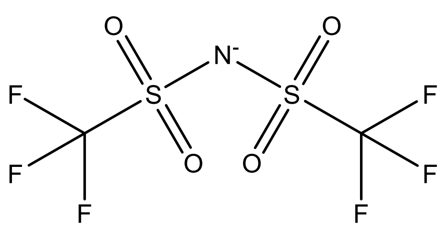
- Viscosity
- Conductivity
- Thermal profile
- Radiolytic properties

Probing the structure of 4-dimethylaminopyridinium (DMAP) ILs

- Cations



- Anion



BIS(TRIFLUOROMETHANESULFONYL)AMIDE

Collaboration with Rutgers University

Nicole Zmich

Physical properties of DMAP versus pyridinium NTf_2 ILs

Cation	Glass transition onset, °C	Melting point °C	Degradation onset, °C	Viscosity, cP, 25 ˚C	Conductivity, mS/cm 25 ˚C
C_4DMAP	-70	27	444	85	2.2
C_4Py	-81	24	388	60	2.2
C_2OC_2 DMAP	-67	None	422	105	1.8
C_2OC_2Py	-80	-18	380	57	2.5

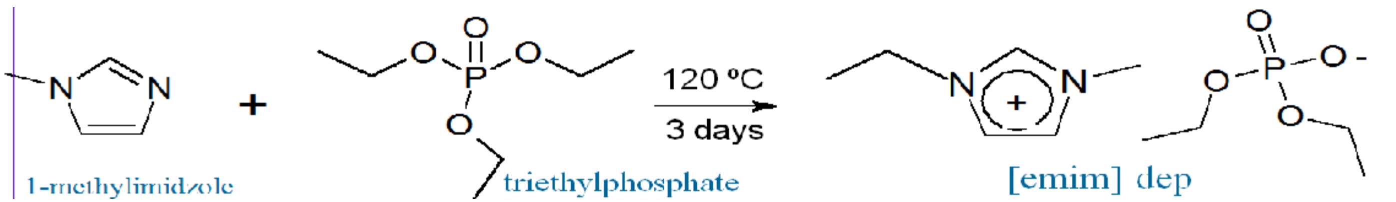
The glass transition temperatures of the DMAP ILs are higher than the pyridinium ILs, making the DMAP viscosities higher as well.

However DMAP salts exhibited higher thermal stabilities and could potentially be useful for high temperature applications

ILs for Pretreatment of cellulose: Biofuel production

Samanta Boursiquot

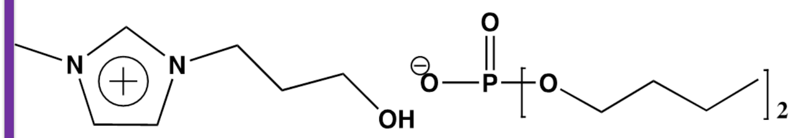
Firmause Payen



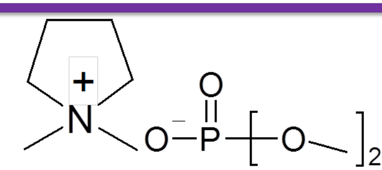
Mariyam Jalees

Alicia Romero

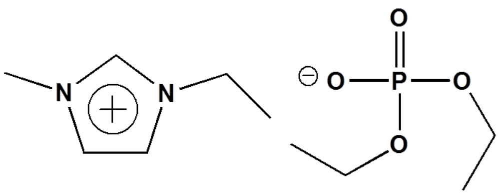
Biofuels: *Bioconversion of lignocellulose to ethanol and butanol facilitated by ionic liquid preprocessing*



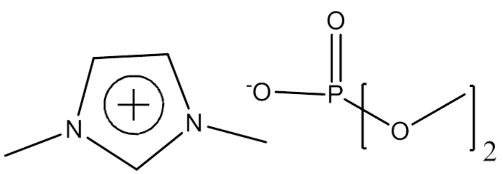
1-(3-hydroxypropyl)-3-methylimidazolium dibutyl phosphate – [C_3OHmim] dbp



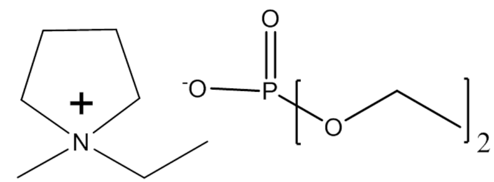
***N,N*-dimethyl pyrrolidinium dimethyl phosphate – [mmPyrr] dmp**



1-ethyl-3-methylimidazolium diethyl phosphate – [emim] dep



1,3-dimethylimidazolium dimethyl phosphate – [mmim] dmp



***N*-ethyl-*N*-methyl pyrrolidinium diethyl phosphate – [emPyrr] dep**

- DAPs can be made halide free in one step and are cheaper that acetate ILs
- Emim DEP dissolved up to 24 wt. % cellulose at 130 °C
- Cellulose is regenerated by adding water to the IL; the IL is recovered by evaporating the water
- DAP ILs dissolve cellulose by breaking up the recalcitrant H-bonded network
- DAPs supports enzyme stability and are less toxic to bacteria than other ILs
- DAP’s are suitable for the pretreatment of lignocellulose and would not impede enzyme saccharification into sugars and bacterial fermentation into alcohols or biofuels.

$1.6 M BNL LDRD 2008-2010

Biofuels: Physical properties of dialkylphosphate ILs

Ionic Liquid	Melting point (^{0}C)	Glass Transition (^{0}C)	Viscosity (20 ^{0}C) (cP)	Density (23^{0}C) (g/mL)	Degradation Point (^{0}C)	Water Content (ppm)
[mmPyrr] dmp	63	-88		solid	231	806
[emim] dep	21	-69	394 @ 26 ° C	1.18	260	333
[emPyrr] dep	Not observed	- 73		1.13	242	511
[mmim] dmp[4]	-	-	363	1.26	263	
[bmim] dbp	-	-	1896	1.04	257	
[C_3OHmim] dbp	Not observed	-68	5878	1.11	248	133

The pyrrolidinium DAPs are more viscous and less thermally stable than the imidazolium DAPs.

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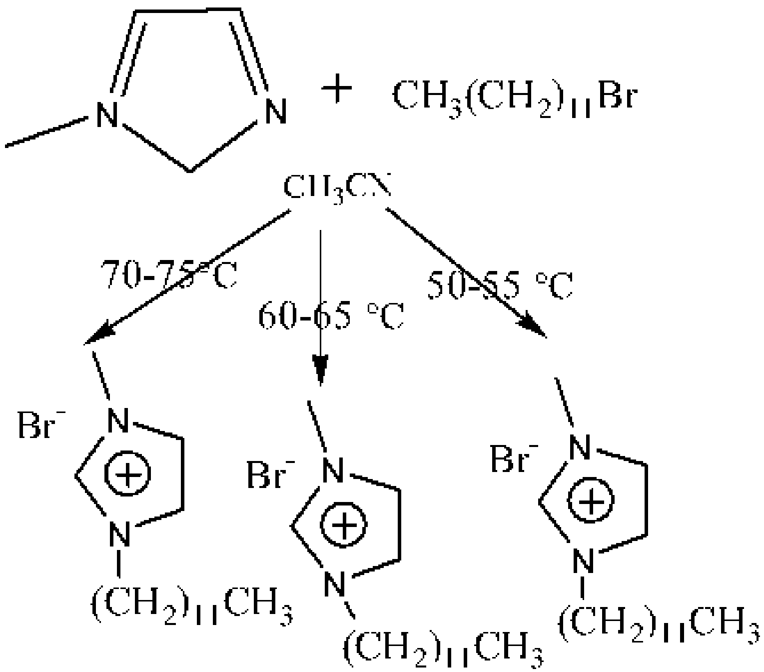
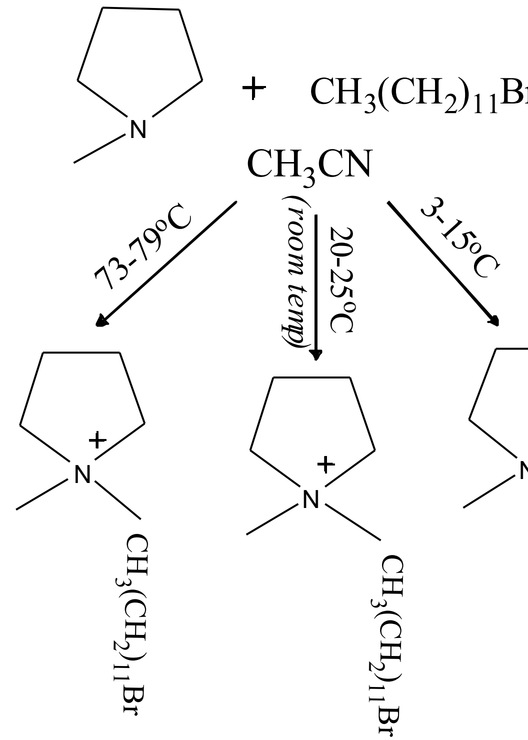
Effect of temperature variation on purity and toxicity

Xing Li





JinHee Gwon

C12MIM Br

C12MIM Br

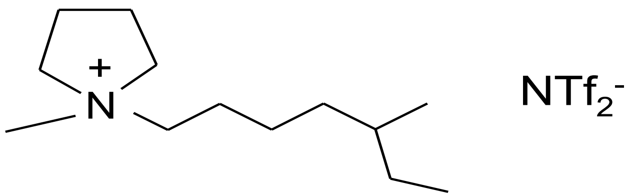
C12MIM Br

P1,12Br

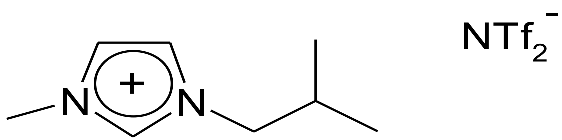
P1,12Br

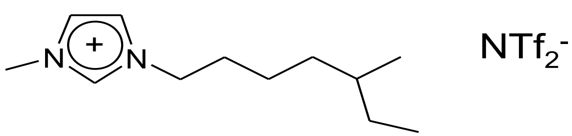
P1,12Br

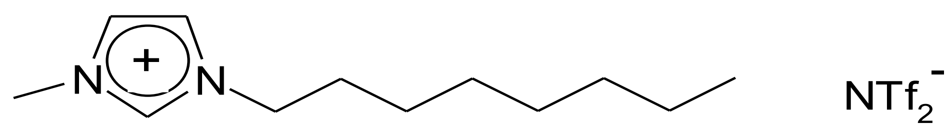
Effect of alkyl chain branching on IL properties




Sharon Ramati





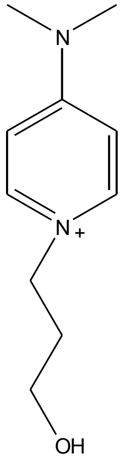


Preliminary result: branched IL much more viscous than linear IL

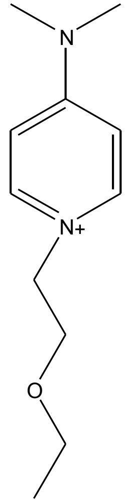
Branched 8C chain IL behaves like the 6C chain IL

Tuning IL properties by structural variation

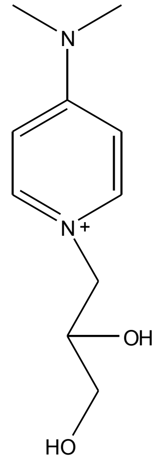
Jasmine Hatcher



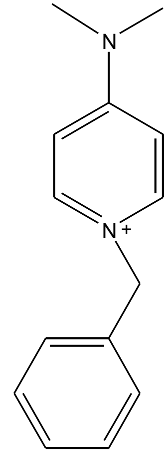
DMAPC3OH



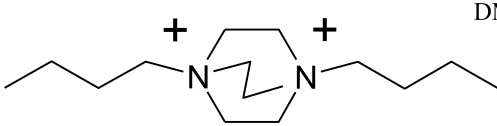
DMAPEOE

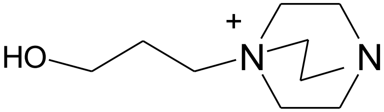


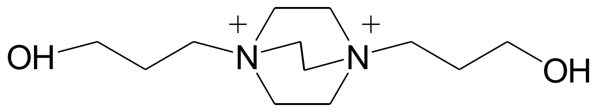
DMAP C3(OH)$_2$

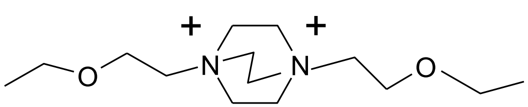


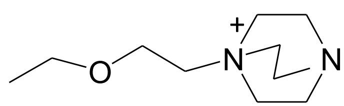
DMAP BEN











Kijana Kerr

M. Thomas, L. Rothman, J. Hatcher, P. Agarkar, R. Ramkirath, S. Lall-Ramnarine, and R. Engel, "Synthesis and Thermochemical properties of Stereoisomeric Dihydroxy- and Tetrahydroxyalkylammonium Salts," Synthesis, 1437-1444 (2009).

Binary mixtures of ILs for Energy Storage Devices

Ionic Liquids in Supercapacitors

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Supercapacitors to the rescue

They call it the Bad Dreamliner because the new Boeing jet has been beset with electrical problems. When new, the Airbus A380 also had electrical problems but they were caught at an early stage. This time it has been more dramatic. In one instance a fire raged in the belly of a Boeing 787 parked at Logan International Airport in the USA. Flames were doused that emanated from the lithium-ion battery compartment. Investigations continue to determine the precise origin of that problem but the air industry is acutely aware that lithium-ion batteries have caused extreme incidents before.

- Supercapacitors are electrochemical storage devices capable of providing high power levels in very short pulses for long periods of time.

- Recently a Boeing Dreamliner plane caught fire because the Li ion Battery overheated.

- Consumers are looking at supercapacitors as safer energy storage devices.

- Traditional electrolyte: organic solvent (Acetonitrile) with a salt dissolved in it. Flammable
- ILS to the rescue – Binary mixtures allow for an extension of the useful properties of ILs

$30 K CUNY Collaborative Grant with Brooklyn College

BROOKHAVEN NATIONAL LABORATORY

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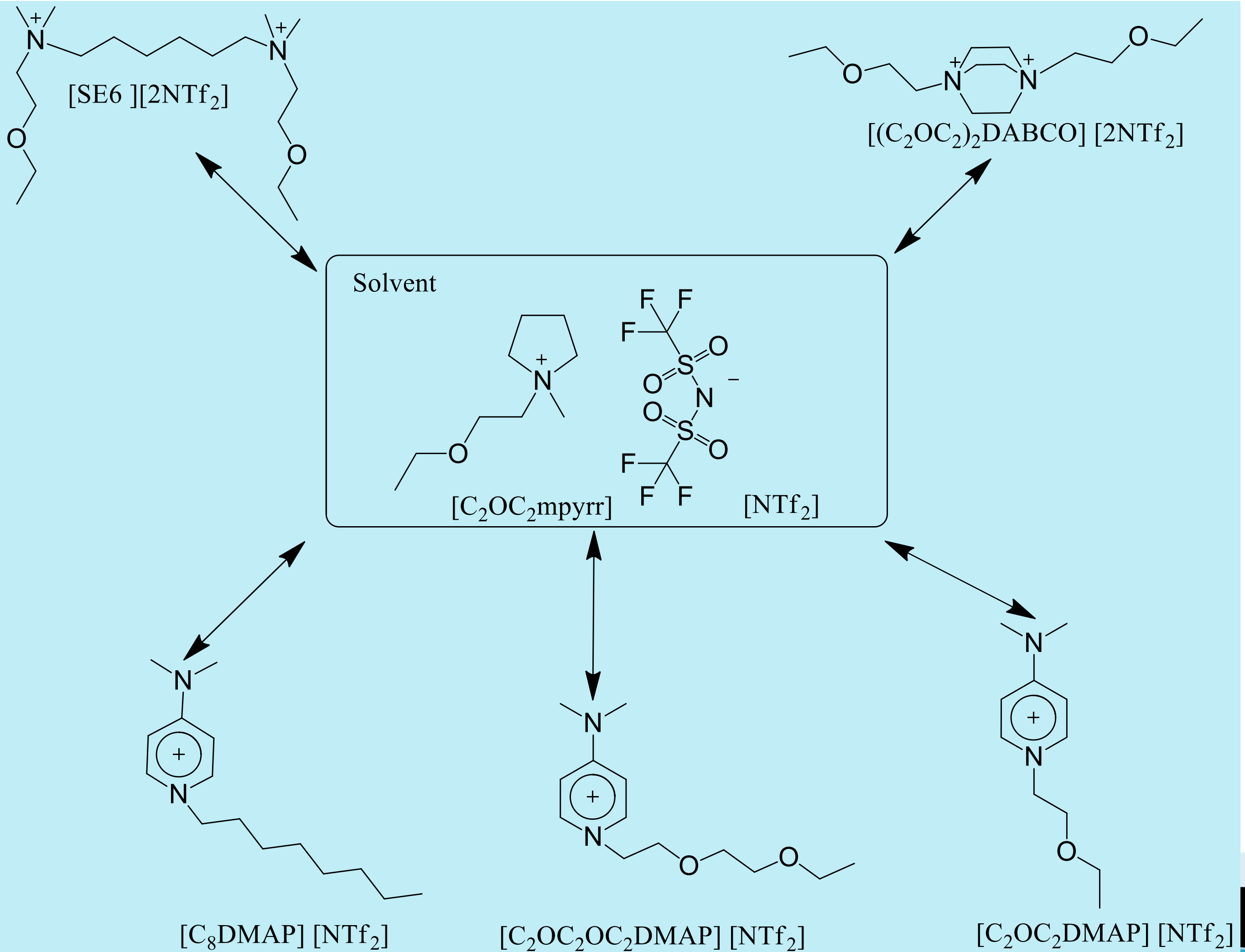
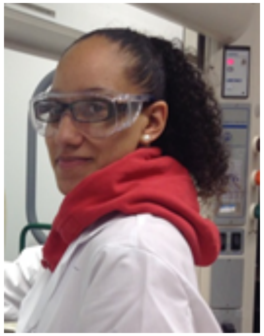
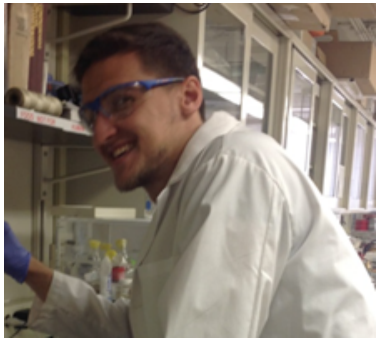
Binary mixtures of ILs for Energy Storage Devices





Emely Rosario



Damian Ewko

S. Lall-Ramnarine, S. Suarez, N. Zmich, S. Ramati, D. Ewko, D. Cuffari, M. Sahin, Y. Adam, E. Rosario, D. Paterno and J. Wishart, Binary Ionic Liquid Mixtures for Supercapacitor Applications. *Journal of Electrochemical Society Transactions*, 2014: *64(4): 57-69*

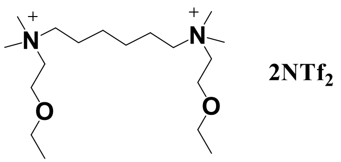
BROOKHAVEN NATIONAL LABORATORY

QUEENSBOROUGH COMMUNITY COLLEGE CUNY

Binary mixtures of ILs for Energy Storage Devices

Physical properties of the NTf_2 salts and mixtures.

Cation(s)	Glass Transition Point, T_g[a] ˚C	Melting Point, T_m[a] ˚C	Degradation Temp, T_d[a] ˚C	Density, g/mL 23 ˚C	Conductivity mS/cm, 25 ˚C	Viscosity Cp 25 ˚C
C2OC2mPyrr	-91	[b]	385	1.41	3.4	53
SE6	-61	[b]	374	1.44	0.2	1582
SE6 + C_2OC_2mPyrr	-88	[b]	384	1.4	2.6	73
$(C_2OC_2)_2$DABCO	[b]	119	292	[c]	-	-
$(C_2OC_2)_2$DABCO + C_2OC_2mPyrr	-88	[b]	377	1.41[d]	8.9*	20
C_2OC_2DMAP	-67	[b]	422	1.41	1.8	106
C_2OC_2DMAP + C_2OC_2mPyrr	-90	[b]	393	1.41	3	57
C_8DMAP	-70	[b]	430	1.29	2.8	135
C_8DMAP + C_2OC_2mPyrr	-90	[b]	390	1.39	2.1	60
$C_2OC_2OC_2$DMAP	-65	[b]	399	1.37	2.1	110
$C_2OC_2OC_2$DMAP + C_2OC_2mPyrr	-89	[b]	393	1.38	2.7	59

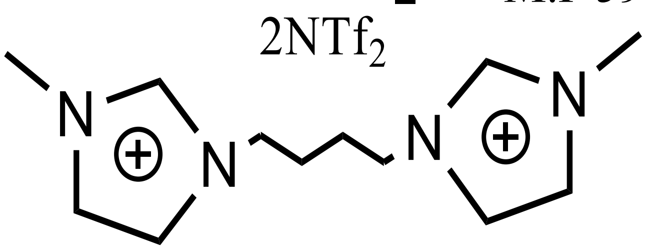


SE6 NTf_2

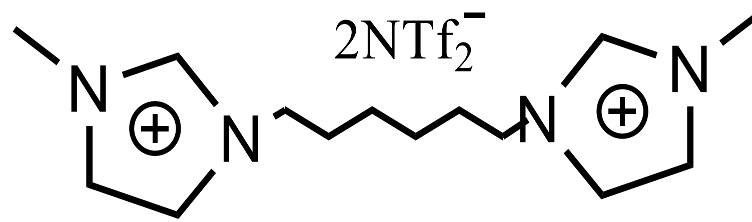
- Mixing ILs can extend their useful properties to greater limits
- The glass transition temperatures can be depressed extending the lower operating temperature limit of these IL systems
- Thermal decomposition temperatures can also be elevated by careful choice of the ions
- No enhancement in conductivity from binary mixtures containing dications, currently working on tailoring the composition of the mixtures

Designing Asymmetric cations for binary IL mixtures

*M.P 59 °C

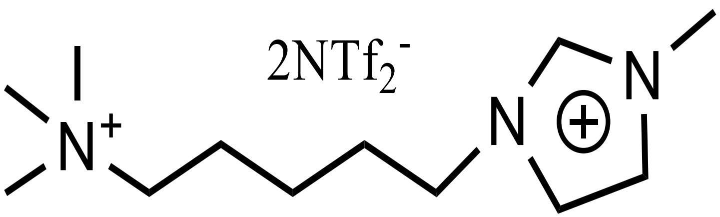


mim C4 mim NTf_2

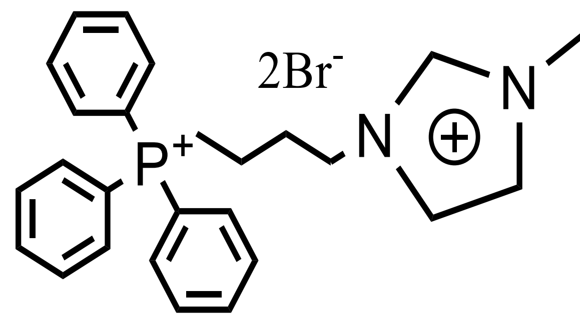


mim C6 mim NTf_2

Eddie Fernandez



$(me)_3N^+$ C_5 mim NTf_2



Ph_3P^+ C_4 mim Br_2

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PSC-CUNY, CUNY COMMUNITY COLLEGE COLLABORATIVE GRANTS AND CUNY COLLABORATIVE GRANTS

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DOE

Department of Energy (Brookhaven National Lab)

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Exploring the Effect of Structural Modification on the Physical Properties of Various Ionic Liquids

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Synthesis, characterization and radiolytic properties of bis(oxalato)borate containing ionic liquids

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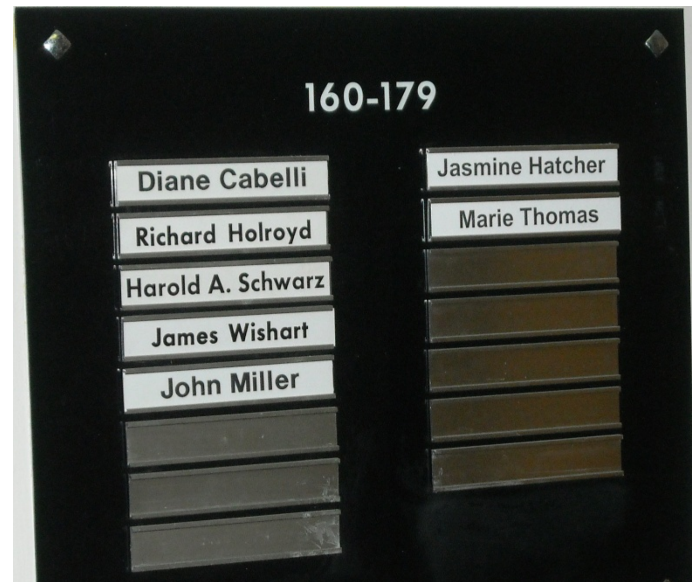

Synthesis 2009, No. 9, 1437–1444

Synthesis and Thermochemical Properties of Stereoisomeric Dihydroxy- and Tetrahydroxyalkylammonium Salts

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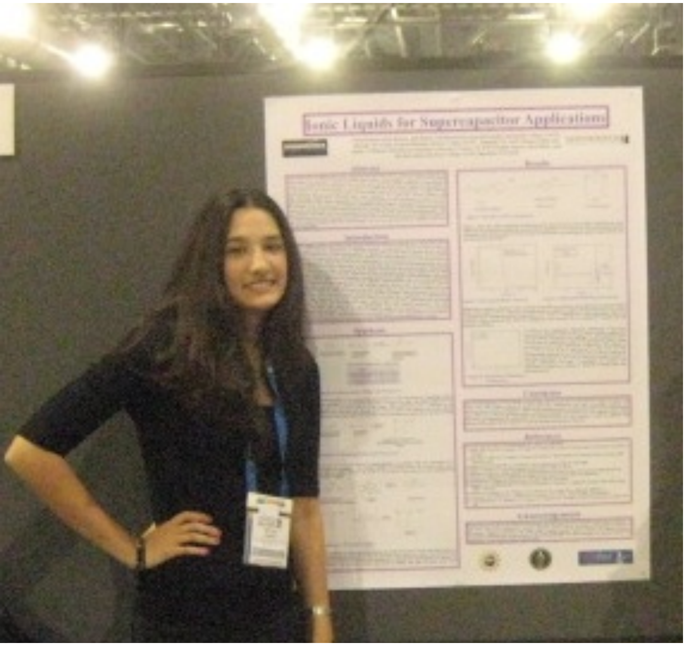
Nicole Zmich



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Binary Ionic Liquid Mixtures for Supercapacitor Applications

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Probing the Physical Properties, Synthesis and Cellulose Dissolution Ability of Dialkyl Phosphate Ionic Liquids

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Published two peer reviewed papers

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